

Predicted field-induced hexatic structure in an ionomer membrane

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Coarse-grained molecular-dynamics simulations were used to study the morphological changes induced in a Nafion[®]-like ionomer by the imposition of a strong electric field. We observe the formation of novel structures aligned along the direction of the applied field. The polar head groups of the ionomer side chains aggregate into clusters, which then form rod-like formations which assemble into a hexatic array aligned with the direction of the field. Occasionally these lines of sulfonates and protons form a helical structure. Upon removal of the electric field, the hexatic array of rod-like structures persists, and has a lower calculated free energy than the original isotropic morphology.

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The transport of protons through an ionomer membrane is at the heart of the operation of a polymer-electrolyte fuel cell. Any procedure that facilitates the transport would thus be of significant value in improving the usefulness of this technology. In this Letter we describe simulations that indicate that application of a strong electric field could change the morphology of an ionomer membrane in such a way as to enhance proton transport appreciably.

The study of proton transport in aqueous ionomers has received considerable attention [1, 2, 3]. For perfluoro-sulfonated ionomer membranes such as Nafion[®] [4] the structure is characterized by a long, hydrophobic, fluorinated main chain, and short side chains terminating in hydrophilic sulfonate anion groups. The dissimilarity between the hydrophobic backbone and the hydrophilic side chain terminations creates a phase-segregated morphology with sharp interfaces between the domains. The sulfonic-acid functional groups aggregate to form a hydrophilic domain that is hydrated upon absorption of water. It is within this continuous domain that ionic conductivity occurs when protons dissociate from their anionic counterions and combine with water to become mobile hydronium ions.

Beginning with a seminal paper by Eisenberg [5], a number of authors have suggested morphological geometries for this microphase separation. These include inverted globular micelles interconnected by a channel structure of cylindrical micelles [6], and lamellar, sandwich-like structures. Other recent approaches are based on micelle-channel [7, 8] and inverted micelle models [9]. There is, however, no complete consensus as to the structure of the percolating networks of sulfonate or water channels.

We have performed simulations of almost-dry Nafion[®]-like ionomers with the goal of determining the morphological changes that would be produced by strong

externally-applied electric fields. We find that the side chains self-organize into cylindrical clusters having their axes parallel to the applied field, and that these clusters form a hexatic array in the plane perpendicular to the field direction. At very strong fields each of the rod-like clusters has an ordered inner core consisting of distinct wires of sulfonate head groups and their attendant protons. The stable cylindrical cluster structures that emerged included an unusual spiral arrangement of three sulfonic wires with four protonic chains. The structural changes resulting from the poling process appear irreversible.

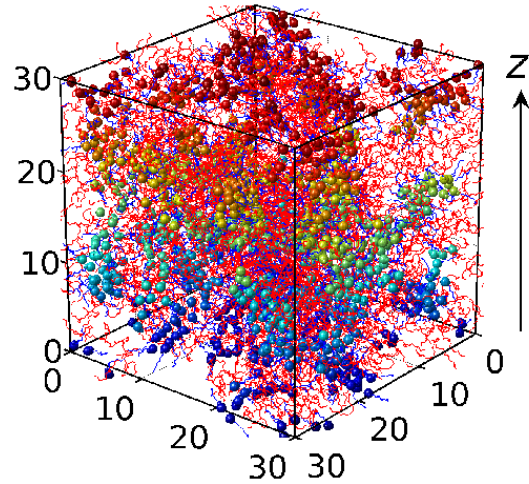


FIG. 1: (Color online) This snapshot shows the ionomer before application of a field. Large/small spheres represent the end-group oxygen/sulfur atoms of the side chains. The colors of the spheres represent altitudes, with blue at the base and red at the top of the simulation box. The size of all structural elements is schematic rather than space-filling.

Model – We employ a united-atom representation for Nafion [10, 11, 12, 13], where the CF_2 and CF_3 groups of the backbone and side chains, and the sulfur atom S and oxygen group O_3 of sulfonate head groups are modeled as Lennard-Jones (LJ) monomers with a universal diameter $\sigma = 0.35$ nm. We assume the number λ of water molecules per sulfonate is small ($\lambda < 5$), and that a proton detached from a sulfonate captures a water molecule and becomes a hydronium ion.

The force-field parameters for the ionomer are chosen to agree in most instances with the Nafion model of Padison [14] and are given in our recent paper [15]. All the partial charges on the ether oxygen, carbon and fluorine atoms of the side chain, and on the fluorocarbon groups of the backbone skeleton are set to zero. Electrostatic charge is located on the sulfur atom (charge $+e$) and oxygen group (charge $-2e$), such that the total charge of the sulfonate head group SO_3^- is $-e$. The hydrogen ion H^+ is considered as part of a hydronium complex of charge $+e$. For the low water contents ($\lambda < 5$) considered in this work, the remaining water molecules are mostly in an immobile state near the pore walls. Therefore one can effectively integrate out their degrees of freedom by introducing a distance-dependent dielectric permittivity [15] and an effective proton diameter σ . Aside from these two approximations, our approach is equivalent to the consideration of a membrane with $\lambda = 1$, when all its sulfonic groups are dissociated forming hydronium ions [16, 17].

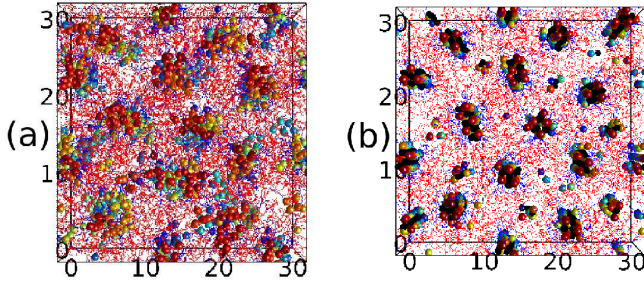


FIG. 2: (Color online) View from above of the simulation system for applied fields of (a) 1.2×10^6 kV/m and (b) $E = 8.2 \times 10^6$ kV/m. Again, a blue color represents a low altitude and a red color a high altitude. Protons are shown as black dots in diagram (b).

The total potential energy of the membrane is taken to be

$$U(\vec{r}) = \sum_i U_b^i + \sum_j U_\theta^j + \sum_m U_\varphi^m + \sum_{k,l} U_{nb}(|\vec{r}_k - \vec{r}_l|) \quad (1)$$

where $(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$ are the three-dimensional position vectors of the N particles in the system. In Eq. (1), i runs over all bonds, j runs over all bond angles, m runs over all torsional angles, and k, l run over all non-bonded (Lennard-Jones and Coulomb) force center pairs in the system. For lightly humidified membrane materials, the protons are mostly energetically bound to their

host sulfonate groups [18, 19]. The resulting $\text{SO}_3^- \text{H}$ effective dipoles have zero net charge, and thus experience no net force in a uniform applied external field, but are subject to torques. Interactions between dipoles are screened with a dipolar screening length R_s [20].

In direct-current experiments, the electrostatic potential $U_{\text{ext}}(\vec{r})$ inside the polymer is considered to be linear [21]. In non-equilibrium molecular dynamic computer simulations the current flow is usually induced by applying an external electrostatic field E [22]. The scalar protonic conductivity χ is defined from the linear relation $\vec{j} = \chi \vec{E}$ between the applied field \vec{E} and the induced current density \vec{j} in the membrane. When the external field is applied along the z -axis, $j = \sum q_i v_{i,z} / V$, where $v_{i,z}$ is the axial component of the velocity of the i -th proton, $i = 1, \dots, N_s$, with N_s the total number of protons and V the sample volume. The conductivity can also be related to the diffusivity D through the Nernst-Einstein relation $\chi = N_s e^2 D / V k_B T$ in equilibrium molecular dynamics simulations. However, this method is less accurate for phase separated systems, where confinement effects, such as proton trapping in the water-sulfonate clusters, strongly affects the overall diffusion constant D .

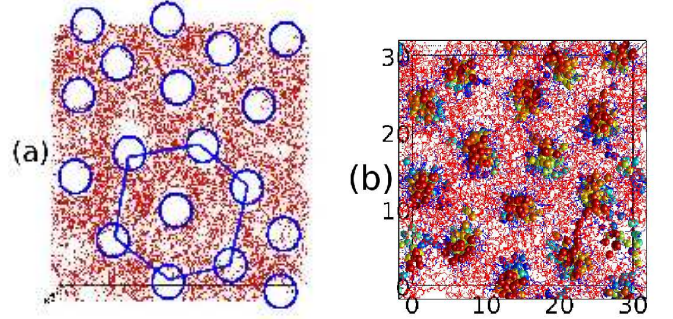


FIG. 3: (Color online) (a) Depiction of only the backbone polymer shows the hexatic array of proton channels formed by the sulfonates. Circles and solid lines are guides for the eye. (b) Remanent structure in a membrane after removal of the applied field.

At low λ we expect surface hopping to be the leading contribution to the current through the membrane. In this case the protons move in the electrostatic energy landscape of the sulfonate ions. Proton transfer is expected to occur at sulfonate-sulfonate separations 0.7-0.8 nm [23] with an energy barrier less than 2.1 kcal/mol [19, 23, 24, 25]. We neglect the contributions to the current arising from Grotthuss and en-masse proton diffusion, which are only significant in highly humidified membranes ($\lambda \geq 5$), and whose evaluation requires full simulations with explicit water molecules.

Simulation results – Molecular dynamic simulations were performed for coarse-grained membranes kept at constant volume $V = (11 \text{ nm})^3$ and constant temperature $T = 300$ K. Each side chain contains 2 hydrophilic and 7 hydrophobic monomers, and there were 14 hydrophobic backbone monomers between adjacent sidechains. The

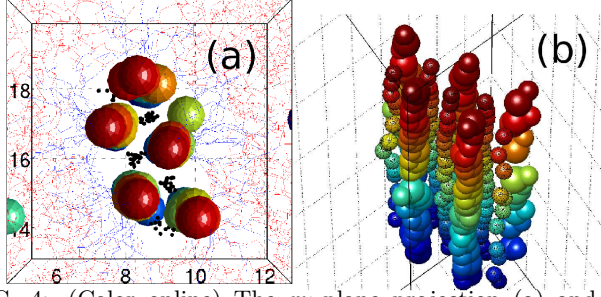


FIG. 4: (Color online) The xy plane projection (a) and a perspective view (b) of a single rod-like cluster with a five-wire structure from Fig. 2(b). Small spheres attached to oxygens represent sulfurs and netted small balls are protons in the right figure.

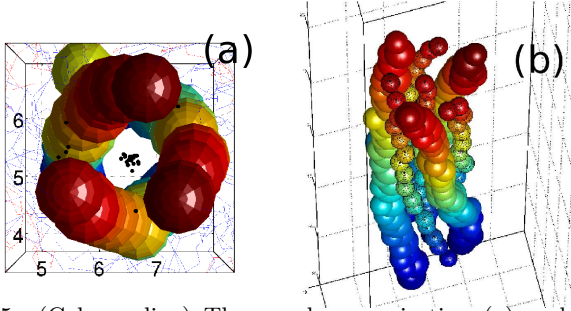


FIG. 5: (Color online) The xy plane projection (a) and a perspective view (b) of a single rod-like cluster with a spiral three-wire structure from Fig. 2(b). Note that there are four protonic wires for a triplet of sulfonic wires.

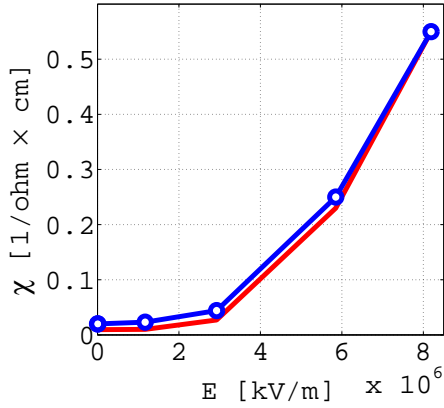


FIG. 6: (Color online) Protonic conductivity χ of the membrane as a function of applied field E . Line without/with circles depicts increasing/decreasing field.

system temperature was controlled by a Langevin thermostat with a friction coefficient $\gamma = 0.1$ and Gaussian noise $6k_B T \gamma$. The equations of motion were integrated using the velocity Verlet algorithm with a time step of 0.2 fs. Periodic boundary conditions and Lekner summation [26] of long-range electrostatic interactions were used.

We temporarily detached the side chains from the

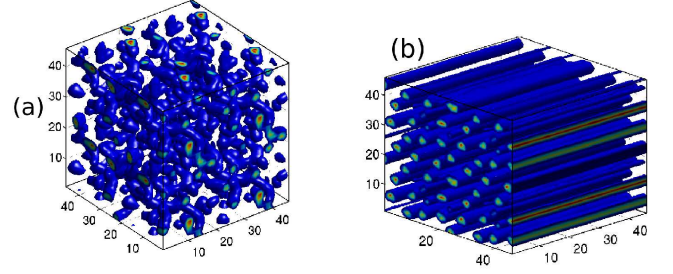


FIG. 7: (Color online) A short-time average of the 3D density distribution of protons for material in zero field (a) and with $E = 8.2 \times 10^6$ kV/m (b).

backbone skeleton [27] and cut the backbone into 14-monomer segments [28] for initial equilibrating runs of 50 ps, after which the polymer was reassembled and equilibrated with another 50 ps run. Statistically averaged quantities were gathered during the next 5-10 ns. A snapshot of a simulated system in the absence of an applied field is given in Fig. 1. The ionomer has undergone a partial phase separation on the nanometer scale into a polymer phase consisting of backbone with pendant side chains and a hydrophilic phase formed by loosely connected clusters of the sulfonate head groups, which are mostly composed of compact multiplets of about 12 sulfonates.

Application of a strong electric field of the order of 10^9 V/m gives rise to the formation of the new morphology illustrated in Fig. 2. The isotropic system of clusters in Fig. 1 is now replaced by a system of cylinders aligned along the z -axis. The sulfonates form the walls of these cylinders, which have a diameter of $\approx 5\sigma$ (≈ 1.8 nm) and a separation of roughly $8-10\sigma$. As the field strength is increased, these cylinders form a hexatic array, as shown in Fig. 3(a). At the same time, the internal structure of the cylinders self-organizes into an array of distinctive ‘wire-like’ chains of sulfonates, or to be more precise, chains of oxygens and sulfurs, and parallel chains of protons. Though the number of sulfonic wires per cylinder varies between 1 and 5, nearly half of the structures have a three-wire structure. All of the other structures observed consist of an equal number of sulfonate and proton wires, an example for a five-wire structure being given in Fig. 4. The mean $\text{SO}_3^- - \text{SO}_3^-$ group spacing along the chains is about 0.65-0.80 nm, which is close to the separation distance expected for Nafion-like membranes [23]. The cylinders composed of three sulfonic wires accommodate four protonic wires, as shown in Fig. 5 for the special case of a spiral cylindrical cluster. The apparent stability of this structure may be an artifact of the periodic boundary conditions.

A remarkable result of the simulations was that this field-induced morphology remains after the removal of the applied field. Fig. 3(b) shows the ordered structure that persists after the field has been removed from the

system shown in Fig. 2(b). In order to understand this phenomenon we calculated and compared the free energies A of the original isotropic structure and the structure with remanent order. The method of thermodynamic integration tells us that the difference ΔA between a system with and without Coulomb interactions is equal to $\int_{\xi=0}^{\xi=1} \langle \partial H(\xi) / \partial \xi \rangle d\xi$ when the coupling parameter ξ characterises the strength of Coulomb interactions U_c^{ij} between head groups i and j . The configurational part of a parametrized Hamiltonian $H(\xi)$ was chosen as $U(\xi, \vec{r}) = K + U(\vec{r}) + (\xi - 1) \sum_{i>j} U_c^{ij}$. The calculated values of $\Delta A / Nk_B T = -9.3$ for the untreated membrane and $\Delta A / Nk_B T = -9.7$ for the treated membrane indicate that the latter has a lower free energy. The morphological changes induced by the strong external field thus appear to be irreversible.

Proton conduction is strongly enhanced by the formation of the sulfonate cylinders along the current direction, as indicated in Fig. 6, which shows that the effective conductivity $\chi(E)$ increases rapidly with field strength. Because the effect of high fields is irreversible, there is hysteresis in the current-field plot. Both the small-field conductivity $\chi = 9.5 \times 10^{-3}$ S/cm of the isotropic membrane and the value of $\chi = 2 \times 10^{-2}$ S/cm for the poled membrane are much smaller than the reported experimental values $\chi = 0.1$ S/cm for humidified Nafion, but much larger than the theoretically predicted surface hopping conductivity $\chi \sim 10^{-5}$ S/cm [29].

The 3D density distribution of protons, plotted in Fig. 7, shows a disordered distribution of protonic clouds inside the isotropic material. In the presence of a strong applied field, however, the protonic clusters connect to each other and form large clusters. These clusters elongate along the field direction, eventually forming rod-like channels.

We thus conclude from our simulations that application of a strong applied electric field to a Nafion[®]-like ionomer may induce the formation of rod-like structures of sulfonate groups, which assemble into a hexatic array aligned with the direction of the field. This novel morphology persists after the removal of the field as a consequence of the lowering of the free energy associated with this change in structure. The induced agglomeration of hydrophilic head groups into long rods appears to reduce the percolation threshold for ion conductance [30]. Simulations also indicate that strong correlations between the sulfonate head groups and protons inside the rods create wire-like structures of charged particles. The geometry of these structures is very rich and includes stable spiral-like three-wire clusters. These effects, if confirmed experimentally, may have an impact on the industrial applications of Nafion-like membranes.

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